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ANALYTIC EQUATION OF STATE FOR SEA WATER

F. H. Fisher, et al

Scripps Institution of Oceanography

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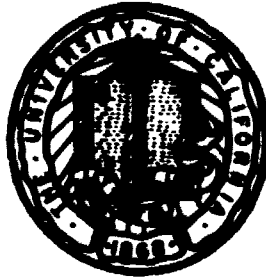
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ANALYTIC EQUATION OF STATE FOR SEA WATER

F.H. Fisher, Robert Bruce Williams and O.E. Dial, Jr.

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20. Abstract

where V is the specific volume, P the pressure, S the salinity and V_{∞} and P_0 are temperature dependent parameters for pure water. In this paper the thermal expansion data of Bradshaw and Schleicher and the sound velocity data of Wilson have been incorporated to yield a new equation of state for sea water. Values of the adiabatic gradient calculated with this equation for $S = 35\text{‰}$ are slightly lower at 2°C than those reported by Pofonoff, for example, 4% at 400 bars and 7% at 1000 bars.

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PREFACE

This work was completed in 1970 and is a sequel to the earlier work in which the Tumlirz equation was selected to represent the properties of pure water as well as sea water. In this paper numerical results have been obtained for the K_1 and K_2 parameters. Millero's group has developed a more accurate and more complex equation of state* for sea water. This equation has been used by some of our colleagues at Scripps and has been found useful in representing properties of sea water.

F. H. Fisher, December 1, 1975

†F. H. Fisher and O.E. Dial, Jr., "Equation of State of Pure Water and Sea Water," SIO Reference 75-28, 1 November (1975).

*F. J. Millero, R. A. Fine, and D. P. Wang, "The Equation of State of Seawater," J. Mar. Res., 32, pp. 433-456, (1974).

ANALYTIC EQUATION OF STATE FOR SEA WATER

F.H. Fisher, Robert Bruce Williams and O.E. Dial, Jr.

University of California, San Diego
 Marine Physical Laboratory of the
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ABSTRACT

Earlier work by Fisher and Dial on pure water and sea water showed the effectiveness of the Tumlirz equation, in representing the precision pure water data of Kell and Whalley from 0 to 150° up to 1000 bars. In addition it was also shown that a modified Tumlirz equation could be used to represent the sea water data of Wilson and Bradley. The equation is

$$V = V_{\infty} - K_1 S + \frac{\lambda}{P_0 + K_2 S + P}$$

where V is the specific volume, P the pressure, S the salinity and V_{∞} , λ and P_0 are temperature dependent parameters for pure water. In this paper the thermal expansion data of Bradshaw and Schleicher and the sound velocity data of Wilson have been incorporated to yield a new equation of state for sea water. Values of the adiabatic gradient calculated with this equation for $S = 35\text{‰}$ are slightly lower at 2°C than those reported by Fofonoff, for example, 4% at 400 bars and 7% at 1000 bars.

INTRODUCTION

Fisher and Dial^{1,2} have re-examined the Tumlirz equation discussed by Eckart³ as an equation of state to represent pure water and sea water. Several equations were examined and the analysis included data from several investigators including the recent precision PV data of Kell and Whalley⁴ on pure water from 0 to 150° and up to 1000 bars. It was found that the Tumlirz equation for specific volume V as a function of pressure P

In attempting to apply this equation to the sea water data of Wilson and Bradley^{5,6} (they also used the Tumlirz equation) Fisher and Dial^{1,2} found an erratic dependence of P_0 , V_{∞} and λ as a function of salinity, S as shown in Figures 1a, b and c. This was also true of the Newton and Kennedy data⁷. However, when λ was constrained to be the value for pure water it was found that both P_0 and V_{∞} displayed a linear dependence on salinity as shown in Figures 2a and b. The linear dependence of the pressure term on S had been suggested by Tammann⁸.

Difficulties were encountered in establishing analytic functions for the temperature dependence of K_1 and K_2 solely from the Wilson and Bradley density data, partly because the data for various salinities were obtained at different temperatures. Also, the results for thermal expansion coefficients did not agree with those obtained by Bradshaw and Schleicher⁹.

In this paper these difficulties have been overcome by making use of the recent

$$V = V_{\infty} + \frac{\lambda}{P_0 + P} \quad (1)$$

provided a fit of ~8 ppm from 0-100° and about 15 ppm from 100-150°.

thermal expansion data of Bradshaw and Schleicher⁹ to determine K_1 and by using Wilson's sound velocity data¹⁰ to determine K_2 ; in the K_2 calculation the recent specific heat data of Bromley et al,¹¹ are also used.

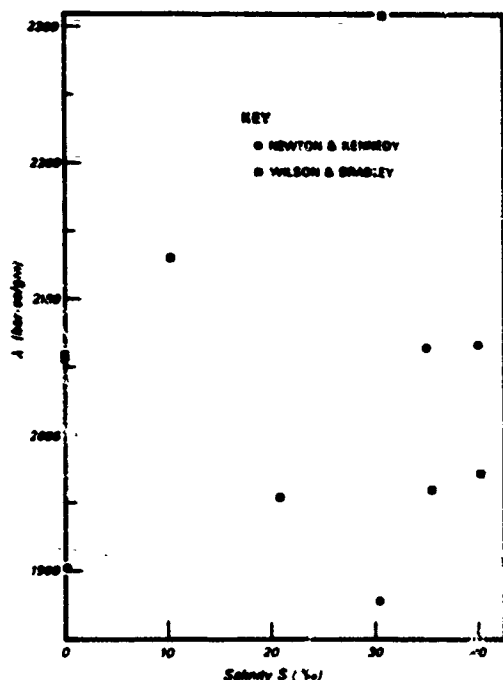


Figure 1a.

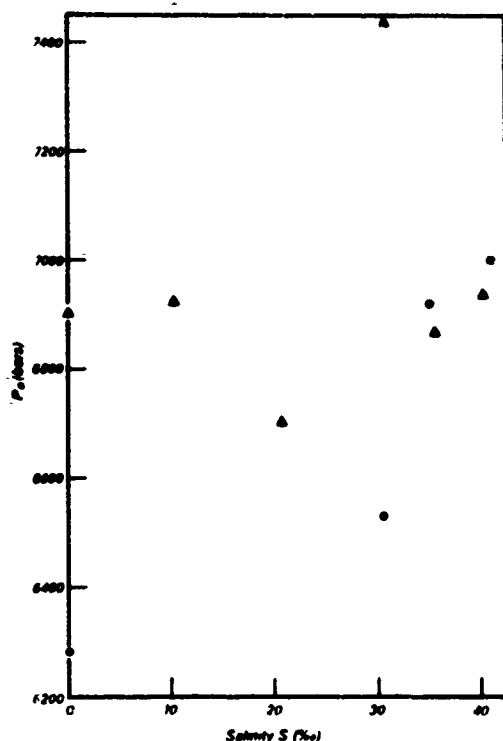


Figure 1b.

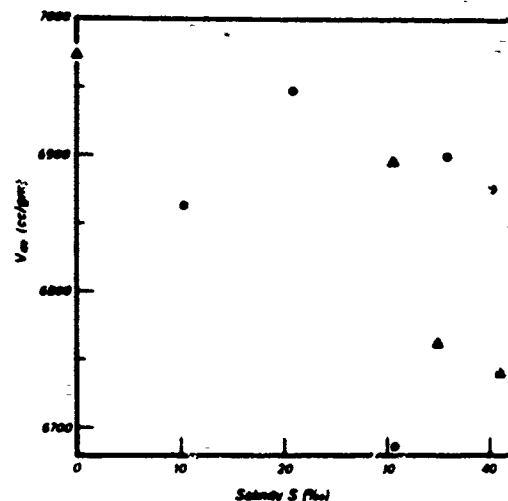


Figure 1c.

Figures 1a, b, and c. Plots of λ , P_0 and V_m for best fit of Tumlirz equation to sea water data at about 10° .

The equation presented here incorporates the most extensive PV data on sea water from a single laboratory (see Table II)^{5,6,7,12,13} as well as the latest thermal expansion data. In addition the equation provides a high precision analytic representation for pure water when the salinity is zero.

Determination of K_1 and K_2

The full equation used to represent pure water from 0 to 150° is shown in Table I. Although the form of equation (1) was determined from fits to the Wilson and Bradley data, difficulties arose in trying to determine K_1 and K_2 from the volume data alone since changes in K_1 could be compensated for by changes in K_2 . However, a determination of K_2 can be made at atmospheric pressure using sound velocity data; this is independent of the PV data as well as K_1 . The isothermal compressibility is

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{V}{C^2} + T \left(\frac{\partial V}{\partial T} \right)_{P,S}^2 / C_P V \quad (2)$$

where V again is specific volume, c the sound velocity, T the temperature (K) and C_p the specific heat at constant pressure. From Equation 1 we find for

$$\beta = \frac{1}{V} \frac{\lambda}{(P_0 + K_2 S + P)^2} \quad (3)$$

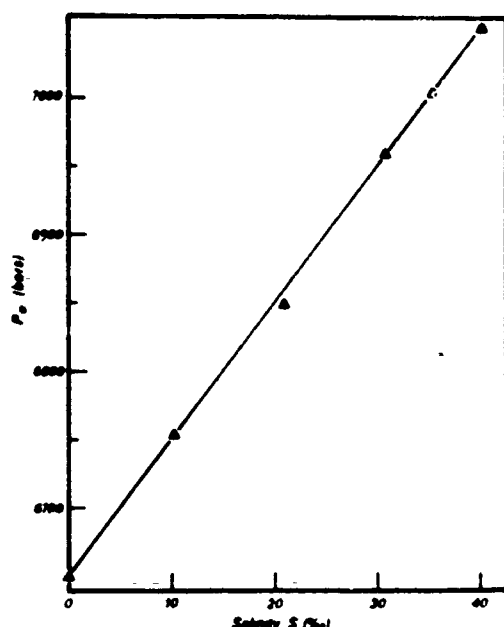


Figure 2a.

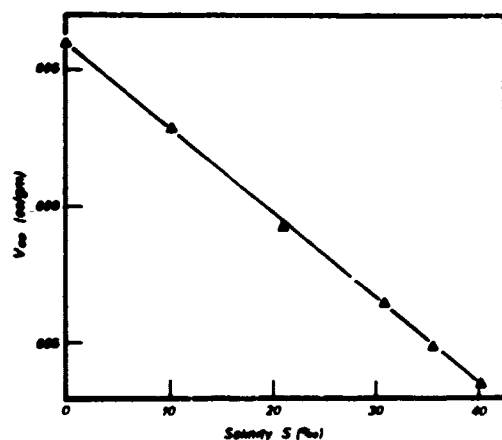


Figure 2b.

Figures 2a and b. Plots of P_0 and V for best fit of Tumirz equation to sea water data at about 10° when λ is constrained to be value for pure water.

and, therefore, at 1 bar

$$K_2 S = -(P_0 + 1) + \left[\frac{\lambda}{V^2/c^2 + T \left(\frac{\partial V}{\partial T} \right)_{P,S} / C_p} \right]^{1/2} \quad (4)$$

The temperature dependence of K was determined by using data for C_p from Bromley⁹, sound velocity from Wilson¹⁰, specific volume from Wilson and Bradley and $(\partial V / \partial T)$ from Bradshaw and Schleicher⁹.

Next, to determine K_1 the thermal expansion data of Bradshaw and Schleicher were used. The general form of K_1 and K_2 as functions of temperature were determined from the Wilson and Bradley PV data to be

$$K_1 = B_0 + B_1 T + B_2 T^2 \quad (5)$$

and

$$K_2 = E_0 + E_1 T \quad (6)$$

By differentiating equation (1) with respect to temperature the only unknown term as a function of temperature is

$$\frac{\partial K_1}{\partial T} = B_1 + 2B_2 T \quad (7)$$

This was evaluated by using the Bradshaw and Schleicher data for $(\partial V / \partial T)_{P,S}$. After this the Wilson and Bradley data was used to find the best values for B_0 .

RESULTS

The temperature dependence of V_0 , P_0 and λ determined from the pure water data are shown in Table I for both the entire $0-150^\circ$ range of the Kell and Whalley data and in a truncated form that is limited to the same temperature range of sea water data. The temperature dependence of both K_1 and K_2 are also shown in Table I. The complete equation for pure water exhibits a density maximum at 4.00° .

Table III shows the fit of our equation in Table I to the Wilson and Bradley data. Although the overall fit is within the precision claimed by Wilson and Bradley it is seen that the low temperature data shows poorer fits than the room temperature data.

Table IV summarizes results of various investigators for the thermal expansion coefficient of sea water shown in the Wilson and Bradley technical report along with our results.

Table V in an analogous manner summarizes the specific volume results.

Similarly, Table VI summarizes the compressibility results.

In Table VII we compare our results for thermal expansion $(\partial V / \partial T)_{P,S}$ against those of B&S as a function of temperature, salinity and pressure. At 0° we find the greatest disagreement with their results, $\sim 10\%$ at 1 bar and $\sim 3\%$ at 1000 bars.

In Table VIII we do see, however, that changes in specific volumes from -2° to 2° calculated by our equation compare very favorably with the results of B&S. In this case we are comparing values from our equation against their raw data.

Table 1

Parameters for Tumlirz Equation for Pure Water and Sea Water.

A. Pure Water, 0 - 100°, 8 ppm and 100 - 150°, 15 ppm Fits to Kell and Whalley Data

$$\lambda = 1,788.316 + 21.55055 T - 0.4695911 T^2 + 3.096363 \times 10^{-3} T^3 - .7541182 \times 10^{-5} T^4$$

$$P_O = 5,918.499 + 58.05267 T - 1.1253317 T^2 + 6.6123869 \times 10^{-3} T^3 - 1.4661625 \times 10^{-5} T^4$$

$$V_{\infty} = .6980547 - .7435626 \times 10^{-3} T + .3704258 \times 10^{-4} T^2 - .6315724 \times 10^{-6} T$$

$$+ .9829576 \times 10^{-8} T^4 - .1197269 \times 10^{-9} T^5 + .1005461 \times 10^{-11} T^6$$

$$- .5437898 \times 10^{-14} T^7 + .169946 \times 10^{-16} T^8 - .2295063 \times 10^{-19} T^9$$

B. Truncated Pure Water 0 - 35°

$$\lambda = 1825.0 + 16.519 T - 0.26157 T^2$$

$$P_O = 5983.4 + 48.685 T - 0.70987 T^2$$

$$V_{\infty} = 0.69520 - 3.412 \times 10^{-4} T + 1.81 \times 10^{-5} T^2$$

$$- 1.67 \times 10^{-7} T^3 + 1.54 \times 10^{-9} T^4$$

C. Sea Water - 2 to 35°, 107 ppm Fit to Wilson and Bradley Data

$$K_1 = 2.679 \times 10^{-4} + 2.02 \times 10^{-6} T - 6.0 \times 10^{-9} T^2$$

$$K_2 = 10.874 - 4.1584 \times 10^{-2} T$$

D. Units

λ bars cc/gm

P, P_O bars

K_2 bar/(0/00)

V_{∞} cc/gm

K_1 cc/gm/(0/00)

S salinity, parts per thousand (0/00)

Table II

Comparison of Density Data at Elevated Pressures for
Pure Water and Sea Water in Temperature Range 0° - 40°.

Name	Temp/Pressure Range/Isotherm Precision	Number of Data Points by:				Total Data Points
		Temp	Pressure	Salinity	Pure Water	
Ekman	0 - 20°/ 600 Bar	5	3	2	1	45
Newton-Kennedy	0 - 25°/1300 Bar/70 ppm	6	13	3	1	312
Wilson-Bradley	0 - 40°/ 965 Bar/20 ppm	9	15	5	1	795
Kell-Whalley	0 - 40°/1026 Bar/5 ppm	8	27	0	1	216
Amagat	0 - 40°/1000 Bar	7	10	0	1	70

Table III

Standard deviations in parts per million of the fit of the FND equation to raw specific volume data of Wilson and Bradley vs temperature and salinity. (Temperature cited is nominal since data were taken at varying temperatures near cited one.) The average of the standard deviations is 107 ppm for all the data.

T S (‰)	10.221	20.720	30.881	35.568	40.370
~ 0°	208	175	230	264	156
~ 5°	173	129	212	187	236
~10°	128	51	167	172	45
~15°	102	38	94	134	55
~20°	42	76	44	140	37
~25°	17	60	85	95	62
~30°	17	106	93	47	104
~35°	22	117	55	43	98
~40°	19	154	34	100	161

Table IV
Thermal Expansion of Sea Water ($S = 35\text{‰}$)
Comparison Tables

T°C	p Bars	Hydrographic Tables $\times 10^5$	Eckart $\times 10^5$	Crease $\times 10^5$	NOL $\times 10^5$	FWD $\times 10^5$
0°	1	5.2	8.0	5.6	7.8	5.76
	200	10.5	13.4	10.6	13.2	10.9
	400	15.4	18.2	15.0	18.0	15.4
	600	19.8	22.5	17.1	22.2	19.3
	800	23.2	26.6	22.6	26.1	22.6
	1000	26.5	29.5	25.6	29.5	25.5
10°	1	16.7	16.2	16.7	16.3	16.6
	200	20.2	19.9	20.1	20.0	20.1
	400	23.5	23.1	23.2	23.3	23.2
	600	26.1	26.0	26.1	26.3	25.9
	800	28.6	28.8	28.6	29.0	28.3
	1000	30.9	30.7	30.8	31.3	30.5
20°	1	25.7	23.8	25.7	24.1	25.6
	200	27.8	26.2	27.7	26.5	27.8
	400	29.8	28.2	29.7	28.6	29.7
	600	31.7	30.0		30.6	31.5
	800	33.5	31.7		32.3	33.1
	1000	35.5	32.9		33.8	34.6
30°	1	33.5	31.3	33.4	31.7	33.1
	200	34.7	32.5	34.6	33.0	34.5
	400	36.1	33.6	35.7	34.2	35.6
	600	37.6	34.4		35.2	36.5
	800	39.3	35.2		36.1	37.5
	1000	41.4	35.8		36.9	38.3
40°	1	41.0	39.4		39.6	40.5
	200	41.8	39.5		40.0	40.7
	400	43.0	39.5		40.2	41.1
	600	44.6	39.5		40.5	41.4
	800	46.9	39.5		40.6	41.7
	1000	49.6	39.5		40.7	42.1

Table V
Specific Volume of Sea Water, ($S = 35\text{‰}$)
Comparison Tables (cm^3/gm).

T°C	P Bars	Hydrographic Tables	Eckart	Crease	NOL	FWD
0°	1	.9726	.9726	.9727	.9726	.9725
	200	.9639	.9640	.9640	.9638	.9638
	400	.9557	.9557	.9558	.9556	.9556
	600	.9479	.9480	.9480	.9479	.9479
	800	.9406	.9407	.9407	.9406	.9406
	1000	.9337	.9338	.9338	.9337	.9337
10°	1	.9737	.9736	.9737	.9738	.9736
	200	.9654	.9654	.9654	.9654	.9653
	400	.9575	.9575	.9576	.9576	.9575
	600	.9501	.9502	.9502	.9502	.9500
	800	.9430	.9432	.9432	.9432	.9430
	1000	.9364	.9366	.9365	.9366	.9363
20°	1	.9758	.9757	.9758	.9757	.9757
	200	.9677	.9678	.9678	.9677	.9677
	400	.9601	.9601	.9602	.9601	.9600
	600	.9528	.9530	.9529	.9529	.9528
	800	.9460	.9462	.9461	.9461	.9459
	1000	.9395	.9397	.9394	.9396	.9394
30°	1	.9787	.9784	.9789	.9784	.9786
	200	.9708	.9706	.9709	.9706	.9707
	400	.9632	.9631	.9632	.9631	.9632
	600	.9561	.9560	.9560	.9560	.9560
	800	.9494	.9493	.9491	.9493	.9492
	1000	.9431	.9430	.9424	.9429	.9428
40°	1	.9823	.9819		.9819	.9822
	200	.9745	.9741		.9741	.9744
	400	.9760	.9666		.9667	.9669
	600	.9601	.9596		.9596	.9598
	800	.9535	.9529		.9529	.9530
	1000	.9473	.9466		.9466	.9466

Table VI

Compressibility of Sea Water, $S = 35\text{‰}$ (Bars⁻¹)
Comparison Tables

T°C	P Bars	Hydrographic Tables x 10 ⁶	Eckart x 10 ⁶	Crease x 10 ⁶	NOL x 10 ⁶	FWD x 10 ⁶
0°	1	46.2	46.5	46.4	46.7	46.5
	200	44.0	44.2	44.0	44.1	43.9
	400	41.7	41.7	41.7	41.7	41.7
	600	39.7	39.5	39.6	39.5	39.6
	800	37.8	37.5	37.7	37.5	37.7
	1000	36.2	35.7	35.9	35.7	36.0
10°	1	44.1	44.1	44.1	44.3	44.0
	200	42.0	41.8	41.9	42.0	41.9
	400	39.9	39.7	39.9	39.8	39.9
	600	38.0	37.8	38.1	37.8	38.1
	800	36.4	36.0	36.3	36.0	36.4
	1000	34.9	34.5	34.6	34.5	34.8
20°	1	42.6	42.5	42.7	42.7	42.6
	200	40.6	40.5	40.6	40.5	40.6
	400	38.7	38.5	38.7	38.5	38.8
	600	36.9	36.7		36.7	37.0
	800	35.5	35.0		35.0	35.4
	1000	33.9	33.4		33.4	33.9
30°	1	41.8	41.6	41.9	41.7	41.7
	200	39.8	39.6	39.8	39.7	39.8
	400	37.9	37.8	38.0	37.8	38.1
	600	36.1	36.1		36.0	36.4
	800	34.4	34.4		34.4	34.8
	1000	32.9	32.9		32.8	33.4
40°	1	41.4	41.5		41.2	41.4
	200	39.5	39.5		39.5	39.5
	400	37.2	37.5		37.4	37.7
	600	35.5	35.8		35.7	36.1
	800	33.4	34.5		34.1	34.5
	1000	31.6	32.8		32.6	33.1

Table VII

Comparison of Values of $\left(\frac{\partial V}{\partial T}\right)_{P,S}$ in parentheses calculated from FWD Equation with Those of Bradshaw and Schleicher Computed from Their Comprehensive Formula.

$\left[\left(\frac{\partial V}{\partial T}\right)_{P,S} \times 10^6\right] \frac{\text{cm}^3}{\text{g}^\circ\text{C}}$								
$S = 30.50^\circ/\text{°}$								
$\frac{TC}{P, \text{bars}}$	0		10		20		30	
1	(43)	39	(154)	154	(246)	246	(325)	324
500	(159)	158	(230)	229	(291)	290	(345)	346
1000	(235)	240	(284)	284	(324)	323	(362)	362
$S = 35.00^\circ/\text{°}$								
$\frac{TC}{P, \text{bars}}$	0		10		20		30	
1	(56)	52	(162)	162	(250)	251	(327)	327
500	(166)	166	(234)	234	(293)	293	(346)	347
1000	(238)	244	(285)	286	(325)	325	(361)	363
$S = 39.50^\circ/\text{°}$								
$\frac{TC}{P, \text{bars}}$	0		10		20		30	
1	(68)	65	(169)	170	(254)	256	(329)	329
500	(172)	174	(238)	239	(295)	296	(347)	348
1000	(241)	248	(287)	289	(325)	326	(361)	363

In Table IX we show a comparison of sound speeds calculated from our equation with those reported by Del Grosso¹⁴ along with Del Grosso's comparison of his results with others. Figure 3 shows a plot of these differences which indicate that sound speed calculated from our equation is in general agreement with all data except the latest from Del Grosso.

DISCUSSION

Of special interest to physical oceanographers for stability calculations is

the adiabatic gradient. Values of the adiabatic gradient calculated equation for $S = 35$ were slightly lower than those reported by Fofonoff¹⁵, for example, 4% at 2° and 400 bars and 7% at 2° and 1,000 bars. In addition we also find that the density maximum crosses the freezing point at $S \approx 22\text{‰}$ instead of the usually cited value of $S \approx 25\text{‰}$.

Since Li's equation did not include an expression for the density of water at atmospheric pressure we have not calculated thermal expansion coefficients and other

Table VIII

Calculated values from FWD equation vs BGS observed values for the change in the specific volume of sea water from -2° to +2°. FWD values are listed in parentheses: Units are in 10^{-6} cc/gm.

P bars Salinity ‰	201.5 35.004	401.2 35.005	601.0 35.004	800.9 35.002	1000.8 35.006
T°C					
-2	(-101)	(-269) -277.1	(-352) -356.9	(-415) -424.3	(-467) -480.5
-1	-97.5				
0	(0) 0	(0) 0	(0) 0	(0) 0	(0) 0
+2	(230) 225	(310) 310	(379) 383	(437) 445	(486) 498

Table IX

Comparison of Speed of Sound Values calculated from the FWD Equation of State with those reported by Del Grosso for NRL and NOL data.

T	Wilson (1960) NOL-2	Del Grosso (1970)	FWD
.141	1449.95	1449.61	1449.86
10.000	1490.40	1489.75	1489.98
19.936	1521.96	1521.13	1521.90
29.970	1545.77	1545.42	1546.39
40.027	1564.77	1563.11	1564.37

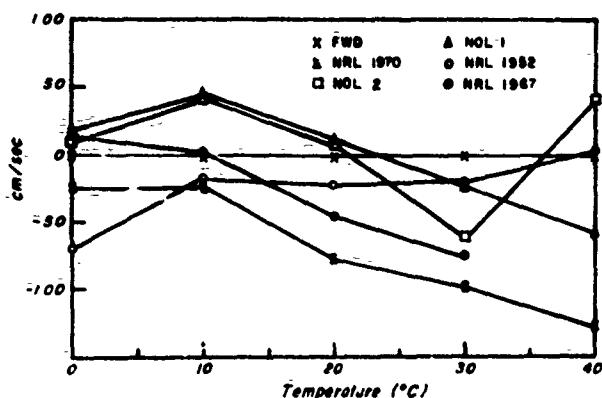


Figure. Comparison of differences in sound speed vs temperature for sea water ($S = 35\text{‰}$) as reported by Del Grosso from values calculated from our equation.

properties from his equation. We did check some specific volumes calculated using his equation and they were within 100 ppm of ours at 30° .

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